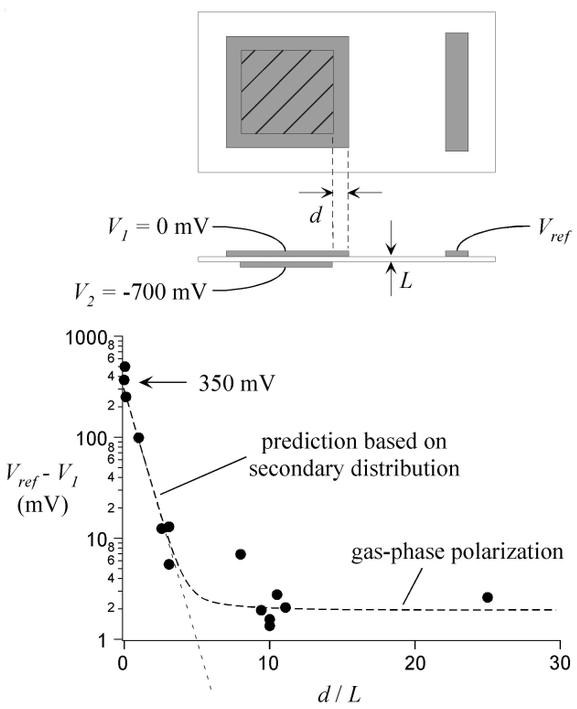
Reference Electrode Placement in Thin Solid Electrolytes

S. B. Adler

Chemical Engineering Department
Case Western Reserve University
10900 Euclid Ave
Cleveland OH 44106-7217

Common experimental wisdom advocates placing a reference electrode as close as possible to the working electrode in order to minimize ohmic contributions to the measured potential. However, within a thin solid electrolyte (as in a fuel cell), variations in potential near an active electrode are often so large that any closely-placed reference electrode will yield highly variable and ambiguous measurements. We report recent numerical calculations of this phenomena and its consequences, including 1) unavoidable "mixing" of counterelectrode response into the working electrode measurement, 2) frequency-dependent "drift" of the ohmic contribution in a.c. impedance measurements, and 3) extreme sensitivity of the measurement to electrode geometry, alignment, and symmetry of the electrode kinetics. We show that these effects make it challenging to measure electrode overpotential accurately on thin cells, and review methods which can used to avoid these ambiguities. We also review an example in which these effects can aggravate (or mitigate) degradation of glass-ceramic seals in a ceramic- electrolyte oxygen generator stack.



Reference Potential vs. Electrode Overhang
(LSCO/Ceria)